

Investigation of the reliability of density functional methods: Reaction and activation energies for Si–Si bond cleavage and H₂ elimination from silanes

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In order to test the reliability of plane-wave and Gaussian-orbital based DFT methods for calculating reaction energies and activation barriers, detailed calculations are performed for several reactions involving gas phase silanes and a simple model of H₂ desorption from the Si(100)2×1 surface. This study is motivated in particular by apparent discrepancies between the results of cluster-model and slab-model calculations of the activation energy for H₂ desorption from the Si(100)2×1 surface. The DFT results obtained with several different exchange-correlation functionals are compared with the results of calculations with the generally reliable QCISD(T) method and, where possible, with experiment. It is found that the functionals usually employed in plane-wave DFT calculations significantly underestimate the activation energies. The Becke3LYP functional, on the other hand, is found to give reaction and activation energies close to experiment and to those from QCISD(T) calculations. © 1996 American Institute of Physics. [S0021-9606(96)00901-3]

I. INTRODUCTION

In recent years a large number of theoretical methods have been used to study the processes of H₂ desorption^{1–11} from the Si(100)2×1 surface and of H-atom diffusion^{12–16} on this surface. *Ab initio* calculations of these processes have been carried out using either slab or cluster models of the surface. The slab models have been used in conjunction with plane-wave density functional theory (DFT),¹⁷ whereas the cluster models have been used in conjunction with the DFT, configuration interaction (CI), and generalized valence-bond CI (GVB-CI) methods. The differences between the activation energies calculated using the slab and cluster models are large enough that researchers using these two models have reached different conclusions concerning the mechanism of H₂ desorption from the monohydride phase of the Si(100)2×1 surface. Three groups using cluster models have obtained barriers for desorption of an H₂ molecule from a single dimer site that are appreciably higher than the measured activation energy, and have concluded that the observed H₂ desorption must occur via a mechanism involving defect sites.^{3,5,7} On the other hand, three recent slab-model/DFT calculations have given activation energies for desorption of an H₂ molecule from a single dimer site close to recent experimental values of the activation energy.^{8–10} We note also that DFT calculations using cluster^{12,15} and slab models^{13,14} give appreciably different activation energies for H-atom diffusion on the Si(100)2×1 surface.

There are several factors that could contribute to the dif-

ferences in the activation energies obtained from cluster-model and slab-model calculations. Table I summarizes the major differences between the two approaches as applied to the calculation of the activation energy for H₂ adsorption/desorption via a process involving a single dimer site on the surface.

In this work we examine several of these factors, with the goal of better understanding the origins of the different reaction and activation energies obtained from the cluster-model and slab-model calculations. In particular, we test the reliability of various exchange-correlation functionals for describing processes involving Si-H, Si-Si, and H-H bond breaking. This is accomplished by comparing the results of DFT calculations, carried out using both Gaussian-orbital and plane-wave basis sets, with those of QCISD(T)¹⁸ and G2¹⁹ level calculations for several reactions involving gas-phase silanes as well as for a simple model for H₂ desorption from the Si(100)2×1 surface. The G2 method has been found to reliably predict reaction energies for a wide range of processes, with the average deviation from experiment for atomization energies being only about 1 kcal/mol.¹⁹ For the processes considered here, it is expected to give reaction and activation energies correct to 3 kcal/mol. The QCISD(T) results should be even more accurate. The DFT and QCISD(T) results for the gas-phase processes are compared with experimental values of the reaction and activation energies where available.

II. PROCESSES CONSIDERED

The gas-phase reactions used in testing the DFT calculations are listed below:

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TABLE I. Comparison of cluster-model and slab-model density functional approaches for studying H₂ desorption from the Si(100) surface.

Computational feature	Cluster model (Ref. 3)	Slab models (Refs. 8–10)
Pseudopotentials	No	Yes
Basis set	Gaussian-type orbitals	Plane-wave
Geometry model	Si ₉ H ₁₄ cluster	Slab model with periodic boundary conditions (5–8 layers; 10–20 Si atoms in unit cell)
Treatment of electron correlation	Becke3LYP functional, QCI	PW91 or BP functionals
Geometry optimization	Analytical gradients	Grid-based searches for TS



Reaction energies were calculated for all four processes, and activation energies were calculated for reactions (1) and (2). In the latter case, both the 1,1- and 1,2-elimination processes were considered. The ¹A₁ ground electronic state was employed for SiH₂. In addition to the gas-phase reactions, a simple Si₂H₆ model is introduced for determining the suitability of various theoretical approaches for calculating the activation energy for H₂ desorption from a single dimer site on the Si(100)2×1 surface.

III. COMPUTATIONAL METHODOLOGY

A. Geometries

The geometries of the reactants, products, and transition state species involved in the gas-phase reactions (1), (3), and (4) were optimized by means of second-order many-body perturbation theory (MP2),^{20–22} correlating all electrons, and using the 6-31G(*d*) basis set.^{23–25} For reaction (2), the MP2/6-31G(*d,p*) optimized geometries of Gordon and co-workers²⁶ were employed. (The 6-31G(*d*) and 6-31G(*d,p*) basis sets are often denoted as 6-31G* and 6-31G**, respectively.) It is well established that MP2 calculations with the 6-31G(*d*) or 6-31G(*d,p*) basis sets generally give geometries in good agreement with experiment.²⁷ The MP2 optimized geometries were used for all subsequent calculations, including those carried out using plane-wave DFT methods.²⁸ This simplifies the calculations as the geometries are fixed, and it eliminates differences in the reaction or activation energies that could result from the geometry differences rather than the differences in method.

For the Si₂H₆ model of H₂ desorption from the Si(100) surface the key geometrical parameters were taken from the calculations on the Si₉H₁₄ cluster model, used in Ref. 3. In particular, the positions of the two Si atoms and of the two adsorbed H atoms are taken to be the same as in the Si₉H₁₄ cluster model. The four remaining H atoms replace the four

Si atoms of the first sub-surface layer of the Si₉H₁₄ cluster, with the angles and dihedral angles specifying the positions of these four H atoms being chosen to be the same as those for the first sub-layer Si atoms of the larger cluster, and the associated SiH bond lengths being reoptimized at the MP2/6-31G(*d*) level of theory. (The geometries of the resulting models for the minimum-energy and transition state species are shown in Figure 1.) The Si₂H₆ cluster model is clearly inappropriate for making quantitative predictions of the activation energy for desorption from the Si(100) surface, and it is introduced primarily to permit the comparison of the results of the various DFT models with those from accurate

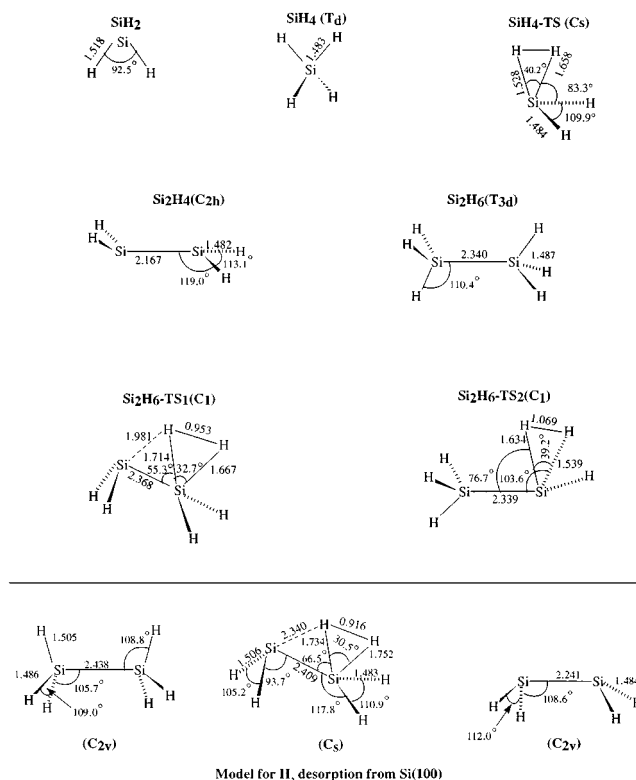


FIG. 1. Geometries of the minimum energy and TS structures of the molecules considered in this study. Bond lengths are in Å. The Si₂H₆-TS₁ and Si₂H₆-TS₂ structures are from Ref. 26; for these species only the geometrical parameters specifying the positions of departing H atoms are given.

many-body calculations, which would be computationally prohibitive for the Si_9H_{14} cluster.

B. DFT calculations

The DFT calculations were carried out using both local and non-local functionals.¹⁷ The local-density calculations were carried out using the Dirac exchange functional²⁹ and either the Perdew–Zunger³⁰ (PZ) or Vosko, Wilk, and Nusair (VWN)³¹ fits to the Monte Carlo data of Ceperley and Alder³² for describing the local correlation functional. The PZ fit was used in the plane-wave calculations and the VWN fit in the Gaussian-orbital calculations.³³ The Becke-LYP (BLYP)^{34,35} non-local exchange-correlation functional was used in both the plane-wave and Gaussian-orbital DFT calculations. In addition, four other non-local functionals were considered. The Becke–Perdew (BP)^{34,36} and Becke3LYP^{37,38} functionals were used in Gaussian-orbital based DFT calculations, and the Perdew–Wang (PW91)³⁹ and CAM(B)-LYP⁴⁰ functionals were used in plane-wave DFT calculations. The BP and BLYP functionals both make use of Becke’s 1988 non-local exchange functional, the former in combination with Perdew’s 1988 non-local correlation functional³⁶ and the latter with the Lee–Yang–Parr (LYP) correlation functional.³⁵ The Becke3LYP functional^{37,38} combines Becke’s 1993 three-parameter “hybrid” exchange functional,⁴¹ which is a linear combination of Dirac’s local, Becke’s 1988 non-local, and exact (i.e., Hartree–Fock) exchange terms and a linear combination of the VWN and LYP correlation functionals. The CAM(B)-LYP functional combines the LYP correlation functional with the CAM(B) modification⁴⁰ of Becke’s 1988 exchange functional. There are two different Perdew–Wang functionals in use; the PW91 functional³⁹ is the more recent (1991 vintage) of these. The Becke3LYP, BP and PW91 functionals are of particular interest because they were used in the recent studies^{2,3,8–10} of the desorption of H_2 from the $\text{Si}(100)2\times 1$ surface (with the BP and PW91 functionals being used in the slab-model calculations and the BP and Becke3LYP functionals being used in the cluster-model calculations). There is a growing body of evidence^{3,12,38,40,42,43} that the newer exchange-correlation functionals incorporating the LYP correlation functional generally give more accurate energy differences than do the BP and PW91 functionals. We are unaware of previous applications of BLYP and CAM(B)-LYP functionals in plane-wave based DFT calculations. The Becke3LYP functional requires explicit evaluation of exchange integrals, which would be computationally prohibitive for with plane-wave basis sets.

The Gaussian-orbital based DFT calculations, as well as the many-body calculations, discussed below, were carried out using the GAUSSIAN 92 program.⁴⁴ The plane-wave DFT calculations were carried out using a Car and Parrinello molecular dynamics approach⁴⁵ to solve the electronic structure problem.

The following basis sets were used in the Gaussian-orbital based DFT calculations: 6-31G(*d,p*),^{23–25} 6-31+G(*d,p*), 6-311G(*d,p*),^{46,47} 6-311+G(2*d,p*),⁴⁸

6-311+G(3*df,2p*),⁴⁸ and 6-311++G(3*df,2pd*).⁴⁸ The 6-31G and 6-311G basis sets provide, respectively, double-zeta and triple-zeta descriptions of the valence space. A single “+” indicates that a set of diffuse *s* and *p* functions is added to each Si atom, whereas a “++” indicates that the basis set includes as well a diffuse *s* function on each H atom.^{48,49} The types of polarization functions are indicated in parentheses, with the first entry giving the number and types of polarization functions on the Si atoms, and the second entry giving the number and type of polarization functions included on the H atoms. For example, (3*df,2p*) designates the presence of three *d* polarization functions and one *f* polarization function on each Si atom and two *p* polarization functions on each H atom.

In order to facilitate comparison with the plane-wave DFT calculations, Gaussian-orbital based DFT calculations were carried out both at an all-electron level and using the Los Alamos effective core potential⁵⁰ on the Si atoms. With this effective potential only the 3*s* and 3*p* electrons on the Si atoms are treated explicitly. Although one of the main attractions of effective potentials is that they permit the use of smaller basis sets than are required for all-electron calculations, in this work they are used in conjunction with the 6-311G(*d,p*) all-electron basis set. In this way, we can be sure that differences in the reaction (or activation) energies obtained from calculations with and without the effective potentials derive primarily from the use of the effective potentials rather than from differences in the basis sets used in the two sets of calculations.

In plane-wave DFT calculations, the size of the basis set is determined by an energy cutoff, E_{max} , and the size of the periodically repeated cell. Most of the calculations reported here used an E_{max} value of 35 Rydberg, although we also tested values of 50 and 70 Rydberg to examine convergence with respect to that parameter. The molecules were placed in cubic boxes with sides of 12, 20, and 25 a.u. to study convergence with respect to distance between neighboring molecules under periodic boundary conditions, with most calculations being done with the 20 a.u. size cell. In addition, the convergence of the plane-wave expansion for the charge density was tested to investigate the effect of high frequency components of the charge density on the total energy. Calculations were performed with values of 1, 2, and 4 for the ratio of the energy cutoff for the charge density to that for the wavefunction (E_{max}). Use of a ratio of 4, in which case the expansion includes all possible charge density modes arising from the wavefunctions, was necessary to obtain convergence (to 1 kcal/mol) of the reaction and activation energies for the calculations with $E_{\text{max}} = 35$ Rydberg. This was particularly true for the non-local functionals. One **k**-point in the Brillouin zone was used in the **k**-integration.

In order to avoid having to use very large energy cutoffs, plane-wave DFT calculations are necessarily carried out using pseudopotentials for heavy elements. In this work the norm-conserving⁵¹ pseudopotential of Bachelet, Hamann, and Schluter (BHS)⁵² brought to the Kleinman–Bylander form⁵³ was employed for the Si atoms. The *s* and *p* terms in the pseudopotential were treated non-locally, whereas a local

approximation was used for the higher angular momentum components. As with the Los Alamos effective core potential used in the Gaussian-orbital calculations, the BHS pseudopotential for Si “removes” the $1s$, $2s$, and $2p$ core electrons. In calculations using plane-wave basis sets, pseudopotentials are sometimes also employed on hydrogen atoms to cut off the short-range part of the Coulomb potential, enabling the use of a smaller energy cutoff than would be required in treating the full Coulomb interaction. In this work, plane-wave DFT calculations were carried out with and without pseudopotentials on the H atoms. This allows us to determine whether the use of pseudopotentials on the H atoms introduces errors in the reaction and activation energies. The pseudopotential for H was developed using the prescription reported by Troullier and Martins,⁵⁴ with the s component being treated non-locally, and higher angular momentum terms being described in the local approximation.

C. QCISD(T) and G2 calculations

The QCISD(T) method¹⁸ is essentially a coupled-cluster method, which is correct through fourth order in the electron–electron interaction and which sums certain classes of interactions to infinite order. This method, when employed with large, flexible basis sets, is generally capable of yielding reaction energies (and activation energies) correct to about 2 kcal/mol.⁵⁵ However, except for very small systems, QCISD(T) calculations with basis sets of the size needed to attain this accuracy are computationally prohibitive. Even for the Si_9H_{14} cluster, used in prior studies of H_2 desorption from the Si(100) surface,³ it was necessary to make approximations in calculating the QCISD(T) energy differences. Specifically, in order to make the calculations affordable, the Los Alamos effective core potential was employed on the Si atoms and a moderate-size basis set—of valence double-zeta +polarization (DZP) function quality on the adsorbed H atoms⁵⁰ and on the Si atoms⁵⁶ of the top two surface layers and smaller basis sets on the remaining atoms—was adopted. Then, in order to estimate the errors due to the use of the DZP basis set and the effective core potentials, three additional sets of calculations, using fourth-order many-body perturbation theory (MP4(SDQ)),^{20–22} were carried out. (The “SDQ” indicates that fourth-order energy contributions involving single, double, and quadruple excitations were included.) The first retained the effective core potentials and employed the same basis set as used in the QCISD(T) calculations. The second also retained the effective core potential on all Si atoms, but used a valence triple-zeta plus double polarization (TZ2P) basis set on the adsorbed H atoms⁵⁷ and the surface Si atoms.⁵⁸ In the third set of MP4(SDQ) calculations, the two Si atoms of the surface dimer were treated at an all-electron level and using the 6-31G(d) basis set, while retaining the effective core potentials on the other Si atoms. Approximate QCISD(T) (A-QCISD(T)) energies, including corrections for increased basis set flexibility and for the errors introduced by use of the effective core potentials, were then estimated from:

$$E(A\text{-QCISD(T)}) = E[\text{QCISD(T)/EC-DZP}] \\ + \{E[\text{MP4(SDQ)/EC-TZ2P}] \\ - E[\text{MP4(SDQ)/EC-DZP}]\} \\ + \{E[\text{MP4(SDQ)/AE-DZP}] \\ - E[\text{MP4(SDQ)/EC-DZP}]\}, \quad (5)$$

where “AE” and “EC” denote “all-electron” and “effective core” potential, respectively.

Although the primary goal of the present study is to assess the reliability of various DFT procedures, we use this as an opportunity to assess also the reliability of the A-QCISD(T) procedure. To do this we have carried out A-QCISD(T) calculations for reactions (1) - (4) as well as for the Si_2H_6 model for H_2 desorption from the Si(100) surface. In the present application of this approach, the intermediate calculations employing effective core potentials were carried out using a valence DZP or TZ2P basis set on all atoms, and those treating all electrons explicitly were carried out using the 6-31G(d,p) basis set on all atoms.

The G2 method of Pople and co-workers¹⁹ is similar in spirit to the A-QCISD(T) procedure, except that pseudopotentials are not used and more flexible basis sets are employed. The G2 method has the advantage of having been tested on a wide range of reactions, and thus is more suitable than the A-QCISD(T) method for calibrating other theoretical methods. In the present study, the G2 energies are evaluated using the expression given in Ref. 59:

$$E[\text{G2}] = E[\text{QCISD(T)/6-311G}(d,p)] \\ + E[\text{MP2/6-311+G}(3df,2p)] \\ - E[\text{MP2/6-311G}(d,p)] + \Delta + E[\text{ZPE}], \quad (6)$$

where Δ is a correction for higher-order correlation effects and $E[\text{ZPE}]$ is a correction for zero-point vibrational energy (ZPE) contributions (calculated using HF/6-31G(d) harmonic frequencies reduced by 10% to correct approximately for electron correlation and anharmonicity effects⁶⁰). The first three terms may be viewed as providing an estimate of the energy at the QCISD(T)/6-311+G(2df,2p) level of theory. Δ provides an estimate of the additional electron correlation which would be recovered upon further expansion to a complete basis set, and is expressed as $A*N_\alpha - B*N_\beta$, where $A = 0.00510$ a.u., $B = 0.00019$ a.u., and N_α and N_β give the numbers of valence α and β electrons, respectively.⁵⁹ For reactions in which the number of electron pairs is conserved, $\Delta = 0$. In discussing results obtained from the G2 approach, ZPE corrections will not be included, except when comparison is made with experiment.

Equation (6) is actually an approximation to the original G2 procedure,¹⁹ in which the influence of diffuse functions and additional polarization functions were considered separately and in which the MP4(SDQ) method was used for evaluating the energy changes due to increased basis set flexibility. The errors introduced in the G2 energies due to the adoption of the computationally less demanding procedure given by Eq. (6) are generally less than 1 kcal/mol.⁵⁹

TABLE II. Reaction and activation energies (kcal/mol) calculated at various levels of theory.^a

Method/basis set	(1)		(2)			(3)	(4)	Si(100)/H ₂ model	
	E _{rxn}	E [‡]	E _{rxn}	E ₁ [‡]	E ₂ [‡]	E _{rxn}	E _{rxn}	E _{rxn}	E [‡]
Plane wave ^b									
LSD	69.3	48.0	54.5	71.4	44.1	66.8	81.6	71.2	75.4
PW91	65.1	53.1	51.9	77.6	48.9	61.4	74.9	69.5	80.9
BLYP	61.1	56.7	49.5	82.7	52.9	53.6	65.2	67.8	85.2
CAM(B)-LYP	67.2	56.4	54.5	81.8	52.1	59.3	72.0	72.5	84.9
EC-6-311G(<i>d,p</i>)									
LSD	72.1	49.2	55.5	75.3	46.5	69.8	86.4	71.6	79.2
BP	65.0	53.9	50.5	81.5	51.2	60.6	75.1	68.3	84.9
BLYP	62.5	56.8	49.5	85.2	54.1	55.1	68.1	67.9	87.9
Becke3LYP	65.7	60.6	54.5	90.0	57.4	57.9	69.1	74.7	92.3
6-311G(<i>d,p</i>)									
LSD	69.0	47.9	53.8	72.6	44.7	66.7	81.9	70.1	76.9
BP	59.4	52.1	48.0	77.6	49.0	55.7	67.0	66.0	81.3
BLYP	56.1	54.3	46.1	80.7	51.5	49.9	59.9	64.7	83.7
Becke3LYP	59.4	58.3	51.2	85.5	54.7	52.5	60.7	71.8	88.2
6-311++G(3 <i>df,2pd</i>)									
LSD	69.1	47.0	54.4	71.0	43.8	67.1	81.7	70.9	75.1
BP	59.7	51.6	48.3	76.3	48.2	56.1	67.5	66.0	79.4
BLYP	56.5	54.1	46.8	79.8	51.1	50.3	59.9	64.8	82.1
Becke3LYP	59.8	58.0	51.8	84.6	54.2	53.0	61.0	71.9	86.7
QCISD(T)/EC-DZP ^c									
MP4(SDQ)/EC-DZP ^c	70.1	65.6	60.6	99.0	61.8	59.6	69.1	78.3	101.7
MP4(SDQ)/EC-TZ2P ^c	65.1	63.5	55.9	94.5	59.3	57.7	66.8	74.7	96.0
MP4(SDQ)/DZP	62.2	63.3	56.1	93.6	59.2	52.8	58.9	74.8	95.9
A-QCISD(T)/TZ2P	56.1	59.9	48.4	87.3	55.5	50.4	57.9	65.0	88.6
QCISD(T)/6-311G(<i>d,p</i>)									
MP2/6-311G(<i>d,p</i>)	63.2	64.3	54.9	92.9	58.6	56.2	64.4	75.2	95.5
MP2/6-311++G(3 <i>df,2pd</i>)	62.1	61.8	52.5	88.5	55.3	57.8	67.4	72.1	90.1
G2 (without ZPE)	58.9	59.6	49.5	87.3	54.6	54.6	64.2	64.6	88.7
QCISD(T)/6-311++G(3 <i>df,2pd</i>)									
MP2/6-311++G(3 <i>df,2pd</i>)	63.5	61.8	54.1	88.6	55.4	57.8	67.2	73.7	90.6
E-QCISD(T)	60.3	60.0	52.0	87.8	55.4	54.5	62.8	68.7	90.4

^aWithout zero-point energy correction.^bThe plane-wave calculations were carried out using a 35 Rydberg energy cutoff and a cubic box with 20 a.u. sides, with periodic boundary conditions.^cGaussian-orbital calculations using the Los Alamos effective-core potential (Ref. 50).

The systems considered here are small enough that full QCISD(T) calculations with the 6-311++G(3*df,2pd*) basis set can be performed, and we have undertaken such calculations in order to better assess the reliability of the various methods. We have also calculated, in the MP2 approximation, energy changes associated with the expansion of the basis set from 6-311++G(3*df,2pd*) to 6-311++G(3*df,2pd*). The motivation for expanding the basis set is to obtain a more balanced description of the H and Si atoms than is provided by the 6-311++G(3*df,2pd*) basis set which is biased toward the Si atoms. These energy changes are used to obtain extrapolated QCISD(T) (E-QCISD(T)) energies:

$$E(\text{E-QCISD(T)}) = E[\text{QCISD(T)/6-311++G(3df,2pd)}] + \{E[\text{MP2/6-311++G(3df,2pd)}] - E[\text{MP2/6-311++G(3df,2pd)}]\}. \quad (7)$$

The errors in the reaction and activation energies obtained

using the E-QCISD(T) procedure rather than from full QCISD(T)/6-311++G(3*df,2pd*) calculations are expected to be less than 0.3 kcal/mol.

IV. RESULTS AND DISCUSSION

Table II reports the reaction and activation energies obtained with a subset of the computational methods considered. In particular, this table includes the results of the DFT calculations using both plane-wave and Gaussian-orbital basis sets as well as the results obtained using the A-QCISD(T) and E-QCISD(T) methods. Table II also reports the results of the intermediate calculations used in obtaining the A-QCISD(T) and E-QCISD(T) energies. The plane-wave DFT results reported in this table are those obtained with a 35 Rydberg energy cutoff and a box with sides of 20 a.u. For the Gaussian-orbital based DFT calculations, results are reported for the 6-311G(*d,p*) and 6-311++G(3*df,2pd*) basis

TABLE III. Dependence of the reaction and activation energies (kcal/mol) calculated in the LSD and Becke3LYP approximations, on the basis set.

Method	(1)		(2)			(3)	(4)
	E_{rxn}	E^\ddagger	E_{rxn}	E_1^\ddagger	E_2^\ddagger	E_{rxn}	E_{rxn}
LSD							
6-31G(<i>d</i>)	69.6	51.4	54.9	77.2	48.2	67.6	82.3
6-31++G(<i>d,p</i>)	68.4	48.4	54.1	73.1	45.2	67.2	81.5
6-311G(<i>d,p</i>)	69.0	47.9	53.8	72.6	44.7	66.7	81.9
6-311+G(<i>2d,2p</i>)	68.6	47.3	54.1	71.1	43.6	66.4	80.9
6-311+G(<i>3df,2p</i>)	68.9	47.2	54.0	70.7	43.3	66.6	81.5
6-311++G(<i>3df,2pd</i>)	69.1	47.0	54.4	71.0	43.8	67.1	81.7
Becke3LYP							
6-31G(<i>d</i>)	59.6	61.4	52.0	90.1	57.9	53.6	61.2
6-31++G(<i>d,p</i>)	58.7	58.6	51.4	86.1	55.1	53.2	60.6
6-311G(<i>d,p</i>)	59.4	58.3	51.2	85.5	54.7	52.5	60.7
6-311+G(<i>2d,2p</i>)	59.1	58.1	51.4	84.6	54.0	52.3	60.1
6-311+G(<i>3df,2p</i>)	59.5	58.1	51.4	84.4	53.9	52.7	60.9
6-311++G(<i>3df,2pd</i>)	59.8	58.0	51.8	84.6	54.2	53.0	61.0

sets. For the former basis set, results are reported both with and without use of effective core potentials, whereas for the larger basis set only the results of all-electron DFT calculations are reported.

Tables III and IV provide additional information on the sensitivity of the results of the Gaussian-orbital calculations to the basis set used, and Table V summarizes the errors introduced into the LSD, BLYP, and MP4(SDQ) reaction and activation energies upon adoption of the Los Alamos effective core potential on the Si atoms. Table VI reports the "errors" in the reaction and activation energies calculated with the various theoretical methods. The "errors" are associated with the deviations from the E-QCISD(T) results, which, of course, are themselves subject to small errors. Table VII compares for reactions (1)–(4) the reaction and activation energies obtained from the BP/6-311++G(*3df,2pd*), BLYP/6-311++G(*3df,2pd*), Becke3LYP/6-311++G(*3df,2pd*), G2, and E-QCISD(T) procedures with those derived from experiment.

The energy cutoff and box size (35 Rydberg and 20 a.u., respectively) used for the plane-wave calculations, reported in the tables, are sufficient to give reaction and activation energies converged to better than 1 kcal/mol. This conclusion is based on the results of calculations on (1) and (2) using a larger (25 a.u.) box size and larger values of the energy cut-

off. If pseudopotentials are not used on the H atoms, it is necessary to use an energy cutoff as high as 70 Rydberg to ensure convergence of the energy differences (when using a box size of 20 a.u.). This was established by carrying out plane-wave DFT calculations for SiH₄, SiH₂, and H₂ without use of pseudopotentials on the H atoms. The reaction and activation energies obtained from the calculations without the pseudopotential on the H atoms and employing the 70 Rydberg cutoff agree to within 0.5 kcal/mol with those obtained using pseudopotentials on the H atoms.

In the calculations employing Gaussian basis sets, the activation and reaction energies obtained with the various DFT methods depend less sensitively on the basis set than do those obtained using the wave-function based methods. For example, for reactions (1)–(4) the average absolute difference between the results (reaction and activation energies) obtained from the Becke3LYP calculations with the 6-311G(*d,p*) and 6-311++G(*3df,2pd*) basis sets is only 0.5 kcal/mol, which is about four times smaller than the average difference between the MP2 results with these two basis sets. (Surprisingly, the convergence of the reaction and activation energies with increasing basis set size is somewhat slower with the LSD functional than with the NLSD functionals.) Moreover, in going from the 6-311+G(*3df,2p*) to the 6-311++G(*3df,2pd*) basis set, the energy differences

TABLE IV. Sensitivity of reaction and activation energies (kcal/mol) to the flexibility of the basis set.^a

Method	(1)		(2)			(3)	(4)	Si(100)/H ₂ model	
	E_{rxn}	E^\ddagger	E_{rxn}	E_1^\ddagger	E_2^\ddagger	E_{rxn}	E_{rxn}	E_{rxn}	E^\ddagger
LSD	0.1	-0.9	0.6	-1.6	-0.9	0.4	-0.2	0.8	-1.8
BLYP	0.4	-0.2	0.7	-0.9	-0.4	0.4	0.0	0.1	-1.6
Becke3LYP	0.4	-0.3	0.6	-0.9	-0.5	0.5	0.3	0.1	-1.5
MP2	0.3	-2.5	-0.8	-4.3	-3.2	1.6	2.8	-1.5	-4.9

^aThe tabulated results are obtained by subtracting the reaction (or activation) energies obtained using the 6-311G(*d,p*) basis set from the corresponding energies obtained using the 6-311++G(*3df,2p*) basis set.

TABLE V. Errors in reaction and activation energies (kcal/mol) associated with the use of the Si effective core potential in the calculations using the 6-311G(*d,p*) basis set.^a

Method	(1)		(2)			(3)		(4)		Si(100)/H ₂ Model	
	E _{rxn}	E [‡]	E _{rxn}	E ₁ [‡]	E ₂ [‡]	E _{rxn}	E _{rxn}	E _{rxn}	E [‡]		
LSD	3.1	1.3	1.7	2.7	1.8	3.1	4.5	1.5	2.3		
BLYP	6.4	2.5	3.4	4.5	2.6	5.2	8.2	3.2	4.2		
MP4(SDQ)	7.9	2.3	4.5	5.4	2.6	6.8	10.2	3.5	5.8		

^aThe errors are obtained from the differences between the reaction (or activation) energies from calculations carried out with and without use of the effective core potential.

obtained from DFT calculations using the Becke3LYP functional change by 0.3 kcal/mol or less, while the MP2 reaction energies for the three processes involving H₂ elimination change by 1.4-1.6 kcal/mol. This is due primarily to the improved description of the Si-H bonds in the MP2 calculations with the 6-311++G(3*df*,2*pd*) basis set. The 6-311++G(3*df*,2*pd*) basis set is believed to be sufficiently flexible to give MP2 energy differences converged to 1 kcal/mol for processes involving Si-H bond breaking. The errors due to basis set truncation are likely to be somewhat larger for processes involving Si-Si bond breaking.

As is seen from Table V, adoption of the Los Alamos effective core potentials in the calculations using Gaussian basis sets leads to sizable errors in the reaction and activation energies, with the errors increasing along the sequence: LSD, NLSD, and MP4(SDQ). In the Gaussian-orbital calculations the errors due to the adoption of the effective core potential are nearly the same for the various non-local functionals, and

only the results for the BLYP functional are reported in Table V. In addition, the errors due to the use of the Los Alamos effective core potential are nearly the same in all the wavefunction-based methods, including the Hartree-Fock approximation (not tabulated).

The average absolute difference between the reaction and activation energies calculated in the local density approximation using the plane-wave basis set (and the BHS pseudopotentials) and those calculated using the 6-311++G(3*df*,2*p*) basis set (without effective core potentials) is only 0.3 kcal/mol. This indicates that LSD calculations using plane-wave basis sets (assuming appropriate choices of box size and energy cutoff) are of comparable quality to LSD calculations carried out at an all-electron level and using large Gaussian orbital basis sets.

One of the most surprising conclusions reached upon examination of the results in Table V is that there is a fundamental difference between the LSD calculations using

TABLE VI. Deviations (kcal/mol) of the reaction and activation energies calculated with various methods from the E-QCISD(T) results.^a

Reaction	(1)		(2)			(3)		(4)		Si(100)/H ₂ model	
	E _{rxn}	E [‡]	E _{rxn}	E ₁ [‡]	E ₂ [‡]	E _{rxn}	E _{rxn}	E _{rxn}	E [‡]		
BLYP/plane-wave	-0.8	3.3	2.5	5.1	2.5	0.9	-2.4	0.9	5.2		
BLYP/plane-wave (corr.) ^b	4.8	5.3	5.4	8.2	3.9	4.5	3.9	3.8	8.4		
BLYP/6-311++G(3 <i>df</i> ,2 <i>pd</i>)	3.8	5.9	5.2	8.0	4.3	4.2	2.9	3.9	8.3		
PW91/plane-wave	-4.8	6.9	0.1	10.2	6.5	-6.9	-12.1	-0.8	9.5		
PW91/plane-wave (corr.) ^b	0.8	8.9	3.0	13.3	7.9	-3.3	-5.8	2.1	12.7		
BP/6-311++G(3 <i>df</i> ,2 <i>pd</i>)	0.6	8.4	3.7	11.5	7.2	-1.6	-4.7	2.7	11.0		
CAM(B)-LYP/plane-wave	-6.9	3.6	-2.5	6.0	3.3	-4.8	-9.2	-3.8	5.5		
CAM(B)-LYP/plane-wave (corr.) ^b	-1.3	5.6	0.4	9.1	4.7	-1.2	-2.9	-0.9	8.7		
Becke3LYP/6-311++G(3 <i>df</i> ,2 <i>pd</i>)	0.5	2.0	0.2	3.2	1.2	1.5	1.8	-3.2	3.7		
MP2/6-311G(<i>d,p</i>)	-2.9	-4.3	-2.9	-5.1	-3.2	-1.7	-1.6	-6.5	-5.1		
MP2/6-311++G(3 <i>df</i> ,2 <i>p</i>)	-1.8	-1.8	-0.5	-0.7	0.1	-3.3	-4.6	-3.4	0.3		
MP2/6-311++G(3 <i>df</i> ,2 <i>pd</i>)	-3.2	-1.8	-2.1	-0.8	0.0	-3.3	-4.4	-5.0	-0.2		
A-QCISD(T)/TZ2P	4.2	0.1	3.6	0.5	-0.1	4.1	4.9	3.7	1.8		
QCISD(T)/6-311G(<i>d,p</i>)	0.3	-2.1	0.1	-3.9	-2.5	1.5	1.6	1.0	-3.7		
QCISD(T)/6-311++G(3 <i>df</i> ,2 <i>p</i>)	1.4	0.0	1.6	0.1	0.1	0.0	-0.2	1.6	1.3		

^aThe tabulated results are obtained by subtracting the reaction (or activation) energies obtained in a given procedure from the corresponding E-QCISD(T) results.

^bThese results have been corrected for errors introduced by the use of pseudopotentials on the Si atoms. The correction procedure is described in the text.

TABLE VII. Comparison of E-QCISD(T), DFT, G2, and experimental reaction and activation energies (kcal/mol).^a

	1		2			3	4
	E_{rxn}	E^\ddagger	E_{rxn}	E_1^\ddagger	E_2^\ddagger	E_{rxn}	E_{rxn}
LDA ^b	63.0	44.1	49.2	68.1	41.6	63.1	77.9
BP ^b	53.6	48.7	43.1	73.4	46.0	52.1	63.7
BLYP ^b	50.4	51.2	41.6	76.9	48.9	46.3	56.1
Becke3LYP ^b	53.7	55.1	46.6	81.7	52.0	49.0	57.2
E-QCISD(T)	54.2	57.1	46.8	84.9	53.2	50.5	59.0
G2(MP2) ^c	52.8	56.7	44.3	84.4	52.4	50.6	60.4
G2(MP4) ^{d,e}	53.3		45.5			50.0	58.8
	(54.7)		(47.1)			(50.0)	(58.6)
Experiment	55.3 ^f	55.9 ^f	45.0 ^g		53.3 ^f	52.3 ^f	63.3 ^g

^aAll entries in this table include zero-point vibrational energy contributions.

^bThe DFT results are those obtained with the 6-311++G(3df,2pd) basis set.

^cThe G2(MP2) results are generated using Eq. 6.

^dThe G2(MP4) results are from Ref. 63, and make use of MP4(SDQ) calculations to estimate the contributions due to increased basis set flexibility and also separately evaluate the contributions of extra polarization functions and diffuse basis functions.

^eThe G2 results in parentheses include corrections for going from the 6-311+G(3df,2p) to the 6-311++G(3df,2pd) basis set (obtained from MP2 calculations).

^fFrom Ref. 64, Table I.

^gFrom Ref. 67.

plane-wave basis sets together with the BHS pseudopotentials and those carried out using Gaussian basis sets together with the Los Alamos effective core potential; whereas the former give reaction and activation energies very close to those obtained from the all-electron LSD calculations, the latter do not. There are several differences between the BHS pseudopotential and the Los Alamos effective core potential, probably the most important of which is that the former have been parametrized to reproduce the results of LSD calculations and the latter to reproduce the results of Hartree–Fock calculations.

A rather different situation exists for the impact of the pseudopotentials or effective core potentials in the calculations using non-local density functionals: in this case, the use of the pseudopotentials introduces sizable errors in the calculations using the plane-wave basis set as well as those using Gaussian basis sets, with the errors generally being greater in the calculations using the Gaussian basis sets. This is most readily seen by comparing the results obtained using the BLYP functional, which was used with both types of basis sets. For this functional, the reaction and activation energies obtained from the plane-wave calculations and the Gaussian-orbital calculations using the Los Alamos effective core potential are, respectively, 3.5 and 4.6 kcal/mol higher on average than the corresponding results obtained from all-electron calculations using Gaussian orbitals. (In the plane-wave calculations the non-local corrections were evaluated perturbatively using the LSD densities, whereas in the Gaussian-orbital calculations they were evaluated self-consistently. However, calculations with Gaussian orbital basis sets indicate that this alters the reaction and activation energies by less than 1 kcal/mol.) Although the results obtained with the BLYP calculations both with the plane-wave

basis set in conjunction with the BHS pseudopotentials and with the Gaussian basis sets in conjunction with the Los Alamos effective core potential are in fairly good agreement with the E-QCISD(T) results, this agreement is, in part, fortuitous as the errors due to the inadequacy of the BLYP exchange–correlation functional and those due to the use of the pseudopotential (or effective core potentials) partially cancel.

We can use the results from the Gaussian-orbital calculations to correct approximately for the errors due to the use of the pseudopotentials in the plane-wave calculations. The corrected BLYP/plane-wave energies are given by:

$$\begin{aligned}
 E_c(\text{BLYP/plane-wave}) &= E[\text{BLYP/plane-wave}] + C \cdot \{E[\text{BLYP/6-311G}(d,p)] \\
 &\quad - E[\text{LSD/6-311G}(d,p)] \\
 &\quad - E[\text{BLYP/EC-6-311G}(d,p)] \\
 &\quad + E[\text{LSD/EC-6-311G}(d,p)]\}, \quad (8)
 \end{aligned}$$

where $C = 1.0$ when the correction for the use of pseudopotentials is assumed to be identical to that for the effective core potentials. This correction procedure reduces the average absolute difference between the reaction and activation energies calculated with the BLYP functional and using the plane-wave basis set in conjunction with pseudopotentials and those calculated using the 6-311++G(3df,2pd) basis set (and treating all electrons explicitly) from 3.3 to 1.6 kcal/mol. If the constant “ C ” in Eq. (8) is taken to be 1.7 instead of 1.0, the average deviation between these two sets of results is further decreased to 0.4 kcal/mol. At the present time we do not have a theoretical justification for this larger

scaling factor, and present it as an empirical observation. These results are reported in Table VI with (using $C = 1.7$) and without the correction for errors due to the use of pseudopotentials. This table also gives results for the PW91 and CAM(B)-LYP functionals, employing correction terms identical to the correction used for the BLYP functional.

The PW91 and CAM(B)-LYP calculations give reaction and activation energies that differ appreciably from the E-QCISD(T) results, with the reaction energies being overestimated and the barrier heights being underestimated. After correction for the errors due to the use of pseudopotentials, it is found that both these functionals, in fact, give reaction energies fairly close to the E-QCISD(T) values, but drastically underestimate the activation energies. It is clear from these results that exchange-correlation functionals that are suitable for calculating reaction energies may be unsuitable for calculating activation energies. We note also that the reaction and activation energies obtained from the corrected PW91 results are close to those obtained from BP/6-311++G(3df,2pd) calculations. This is noteworthy because these are the two functionals that have been used in previous plane-wave DFT calculations of the activation energies of H₂ desorption from Si(100).

Of the functionals considered, DFT calculations with the Becke3LYP functional give results closest to those obtained from the E-QCISD(T) procedure. For reactions (1)–(4), the largest “error” in the Becke3LYP/6-311++(3df,2pd) reaction and activation energies is only 3.2 kcal/mol and the average error is only 1.5 kcal/mol. The calculations with the Becke3LYP functional underestimate the activation energies, but by far less than any of the other functionals considered. DFT and QCISD(T) calculations on reaction (1) have been previously reported.⁶¹ The BP and BLYP reaction and activation energies reported there differ by about 3 kcal/mol from those obtained in the present work. Most of these differences are probably due to the use of different geometries in the two studies. The QCISD(T) result of Sosa and Lee⁶¹ differs by less than 2 kcal/mol from our QCISD(T)/6-311+G(3df,2p) result. In this case most of the difference is likely to derive from our use of a somewhat more flexible basis set.

MP2 calculations with the large 6-311++G(3df,2pd) basis set do a credible job of predicting the reaction and activation energies of processes (1)–(4), with the average absolute error (2.2 kcal/mol) being only slightly larger than that for the DFT calculations with the Becke3LYP functional. The average absolute error in the A-QCISD(T) results is 2.5 kcal/mol, but in this case the average error in the activation energies is much smaller than that in the reaction energies (0.2 vs. 4.0 kcal/mol). Thus the A-QCISD(T) procedure appears well suited for calculating activation energies.

For reactions (1)–(4), the G2 reaction and activation energies (without ZPE corrections) agree to within 1.2 kcal/mol of the QCISD(T)/6-311+G(3df,2p) results, confirming the validity of the less computationally demanding G2 procedure. However, for reactions (1) and (2) the G2 and QCISD(T)/6-311+G(3df,2p) reaction energies are 1.4–2.5 kcal/mol lower than the E-QCISD(T) results. As

noted above, this primarily reflects the inadequacy of the 6-311+G(3df,2p) basis set, used in the G2 calculations, for describing the Si-H bond strengths.

The trends are somewhat different for the Si₂H₆ model for H₂ desorption from the Si(100) surface than for reactions (1)–(4). For example, for this model system the Becke3LYP and MP2/6-311++G(3df,2pd) methods overestimate the reaction energies by 3.2 and 5.0 kcal/mol, respectively, and the G2 method underestimates the reaction energy by 4.1 kcal/mol. The larger errors in the Becke3LYP, MP2, and G2 values of the reaction energies for the Si₂H₆ model for H₂ desorption than for reactions (1)–(4) may be due to the partial diradical character of the SiH₂–SiH₂ species formed after H₂ desorption. This problem appears to be less severe for the more realistic Si₉H₁₂ cluster model of the surface,³ perhaps due to the greater electron delocalization in the Si₉H₁₂ model than in the Si₂H₆ model. The problem posed by the diradical character is also less severe for the calculation of the activation energy of H₂ elimination from this model system. The Becke3LYP calculations give a lower barrier height (by 3.7 kcal/mol) and the MP2/6-311++G(3df,2pd) procedure gives a slightly greater barrier height (by 0.2 kcal/mol) than that obtained from the E-QCISD(T) calculations. These results are in line with those found for reactions (1) and (2).

We now turn to the comparison of the calculated and experimentally determined reaction and activation energies for the gas phase reactions. The experimentally derived energy differences include zero-point vibrational energy (ZPE) effects, so in order to compare theory and experiment, corrections for the ZPE contributions must be made to the calculated energy differences. To do this, one-half the sum of the HF/6-31G(d) normal-mode frequencies^{26,62,63} was used, reduced by 10% to correct approximately for errors due to the neglect of electron correlation and anharmonicity effects,⁶⁰ and then added to the energies obtained from the various electronic structure calculations.

Table VII compares the theoretical and experimental results (where available) for reactions (1)–(4). The theoretical results are reported for the following levels of theory: DFT calculations using the BP, BLYP, and Becke3LYP functionals, all using the 6-311++G(3df,2pd) basis set, the E-QCISD(T) method, and the G2 method, in two variants, one based on Eq. (6) and the other using the original formulation, in which the energy changes due to increased basis set flexibility are estimated by means of the MP4(SDQ) method. The latter G2 results are taken from Pople and co-workers.⁶³ The E-QCISD(T) calculations avoid the approximations made in the G2 method and also include a correction for the expansion of the basis set from 6-311+G(3df,2p) to 6-311++G(3df,2pd), and hence are expected to be more accurate than G2 calculations.

For the SiH₄ → SiH₂ + H₂ and Si₂H₆ → Si₂H₄ + H₂ (1,2-elimination) reactions, the G2, E-QCISD(T), and Becke3LYP procedures all give reaction energies within 2.5 kcal/mol of the experimental values.⁶⁴ These three methods also give activation energies for reaction (1) and for (1,1) elimination of H₂ from Si₂H₆ within 1.3 kcal/mol of the

experimental values. As follows from our earlier discussion, the DFT calculations with the BP and BLYP functionals give activation energies for (1) considerably lower than the experimental values.

For reactions (3) and (4), which involve Si–Si bond breaking, G2, E-QCISD(T) and Becke3LYP procedures all give reaction energies lower than the experimental values. With the E-QCISD(T) method, the reaction energies for (3) and (4) are, respectively, 1.8 and 4.3 kcal/mol lower than the experimental values. Similar discrepancies are found for G2 results. The discrepancy between theory and experiment for these reaction energies is 1.5–1.8 kcal/mol larger for the Becke3LYP calculations. Part of this discrepancy between theory and experiment could be due to basis set truncation. However, it could also be partly the result of errors in the experimental values of the reaction energies.

V. CONCLUSIONS

In this work we have presented a detailed comparison of plane-wave DFT, Gaussian-orbital DFT, and high-level E-QCISD(T) calculations for several reactions involving SiH₄, Si₂H₄, and Si₂H₆. The major conclusions reached from this analysis are:

(1) Of the functionals considered, DFT calculations with the Becke3LYP functional most closely reproduce the reaction and activation energies obtained from the E-QCISD(T) procedure, which, in turn, gives results close to experiment. All the non-local functionals considered here prove superior to the local density functional.

(2) DFT calculations with other commonly used non-local functionals, such as the BP or PW91 functionals, underestimate activation energies for H₂ elimination from SiH₄, Si₂H₆, and for a Si₂H₆ model of H₂ desorption from Si(100) by amounts ranging from 5 to 11 kcal/mol. For the Si₂H₆ model for H₂ desorption from Si(100) the BP and PW91 activation energies are, respectively, 9.5 and 11 kcal/mol smaller than the E-QCISD(T) value.

(3) Providing that the box size and energy cutoffs are sufficiently large, plane-wave DFT calculations in the local density approximation (and employing the BHS pseudopotentials) give essentially the same reaction and activation energies as do LSD calculations using large Gaussian basis sets and treating all electron explicitly. This indicates that the errors introduced by the use of the BHS pseudopotentials in the plane-wave LSD calculations sets are small (≤ 1 kcal/mol). In contrast, the use of Los Alamos effective core potentials in Gaussian-orbital LSD calculations introduces significant errors (ranging from 1.3 to 4.5 kcal/mol) in the reaction and activation energies.

(4) The errors introduced into the reaction and activation energies by use of the BHS pseudopotentials in NLSD calculations are as large as 5.6 kcal/mol. In general, somewhat larger errors (up to 8.2 kcal/mol) result from the use of the Los Alamos effective core potential in the NLSD calculations using Gaussian orbital basis sets.

(5) The use of pseudopotentials or effective core potentials in non-local DFT calculations causes the reaction and activation energies to be overestimated (compared to the corresponding results from calculations treating all electrons explicitly). This error acts in an opposite direction from that caused by the deficiencies of the BP, PW91, CAM(B)-LYP, and BLYP non-local functionals, and, as a result, there is partial cancellation of errors when using these functionals with pseudopotentials (at least for the processes studied here). Even so, the activation energies obtained from plane-wave DFT calculations using the PW91 functional are 6–10 kcal/mol too low compared to the E-QCISD(T) results. The errors in activation energies obtained from plane-wave DFT calculations using the BP functional are expected to be comparable.

(6) The A-QCISD(T) method used previously in studies of H₂ desorption from and H-atom diffusion on the Si(100)2 \times 1 surface^{1–3,12} is found to give activation energies in excellent agreement with those from the E-QCISD(T) method.

Plane-wave DFT calculations provide major advantages for the study of reactions on surfaces. However, the results of the present work show that in order to obtain the accuracy required to predict activation energies correct to 2–3 kcal/mol (which is often essential for deciding between different mechanisms) it will be necessary to adopt non-local exchange-correlation functionals that are more reliable than the BP or PW91 functionals that are commonly employed in modeling surface processes, and it will be necessary to develop procedures that minimize the errors due to the use of pseudopotentials. Unfortunately the Becke3LYP functional, which is superior to the other functionals tested in this study, requires evaluation of exchange integrals which precludes its use in plane-wave calculations. Our results indicate that the BLYP functional, although inferior to the Becke3LYP functional, is superior to the BP and PW91 functionals, for calculating activation energies of H₂ elimination from silanes, and we recommend the adoption of the BLYP functional in plane-wave codes.

For the Si₂H₆ model for H₂ desorption from Si(100), plane-wave DFT calculations with the PW91 functional underestimate the activation barrier for H₂ desorption by 10 kcal/mol (as compared with the results of E-QCISD(T) calculations). We expect that the use of the PW91 or BP functionals in the plane-wave slab-model studies of H₂ desorption from the monohydride phase of Si(100) also causes the activation energy for this process to be underestimated by a similar amount. This leads us to question the conclusions reached in Refs. 8–10 about the viability of the “direct” mechanism for H₂ desorption from the Si(100) surface.

Although our studies of activation energies has emphasized H₂ elimination processes, we note that the deficiency of the PW91 and BP functionals for calculating activation energies is likely to be a general phenomenon. We have recently found that the use of these functionals causes the activation energies for H-atom diffusion on Si(100) to be underestimated by 10–15 kcal/mol.⁶⁵

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